

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : <b>C08G 65/32, C08L 71/02, C09D 17/00</b>		A1	(11) International Publication Number: <b>WO 94/18260</b> (43) International Publication Date: 18 August 1994 (18.08.94)
(21) International Application Number: PCT/NL94/00019			(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, HU, JP, KP, KR, KZ, LK, LV, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 27 January 1994 (27.01.94)			
(30) Priority Data: 9300118 9 February 1993 (09.02.93) BE			
(71) Applicant ( <i>for all designated States except US</i> ): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).		Published	<i>With international search report.</i>
(72) Inventors; and			
(75) Inventors/Applicants ( <i>for US only</i> ): DEKKER, Gerrit, Hendrik [NL/NL]; Elsbeek 23, NL-8033 BC Zwolle (NL). HENDRIKS, Johannes, Wilhelmus, Maria [NL/NL]; Van Echtenmarke 4, NL-8016 DB Zwolle (NL). PONS, Dick, Adriaan [NL/NL]; Dreessingel 114, NL-8015 CD Zwolle (NL).			
(74) Agent: SCHMEETZ, Marcel, Max, Hubertina, Johanna; Octroibureau DSM, Postbus 9, NL-6160 MA Geleen (NL).			

(54) Title: WATER-SOLUBLE AND AIR-DRYING RESIN

(57) Abstract

The present invention relates to a water-soluble and air-drying resin. A water-soluble and air drying resin, comprising substantially units of: A. a monoether of a polyethylene glycol having 5-100 ethylene oxide units per molecule, and B. the reaction product of: B1) one or more unsaturated fatty acids or one or more polyalcohol(s) esterified with unsaturated fatty acids with B2) an  $\alpha,\beta$ -ethylenically unsaturated carboxyl compound wherein the molar ratio of A:B is from about 0.2:1 to about 4:1. The resin can amongst others be used as a dispersing agent, in a wood preservative and in a pigment paste.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

### WATER-SOLUBLE AND AIR-DRYING RESIN

5

The present invention relates to water-soluble, air-drying resins and a process for making the same. The 10 present invention further relates to the use of said resins as dispersing agents and as agents for use in wood preservation applications.

Examples of water-soluble resins that can be used as dispersants are described in Paint Flow and Pigment Dispersion, by T.C. Patton (pp. 290-296, 1979). Known dispersants such as for example polyphosphates, isobutylene maleic acid copolymer-sodium salt and polyacrylates cannot be sufficiently mixed with binders like alkyd resin dispersions in order to obtain paints with good gloss properties. It is 20 also possible to use water-dilutable alkyd resins as dispersants for pigments. In order to obtain clear solutions and good properties (i.e. for instance pigment wetting properties), however, the known resins used as dispersants have to be combined with compounds that are undesirable for 25 environmental and medical reasons, such as, for example, amines or organic solvents.

Water-soluble resins which can be used as dispersants are also known from W091/06586. This publication describes a resin which is substantially built up from units 30 of:

- A. a polyethylene glycol with ethylene oxide units,
- B. an allyl ether compound and
- C. the reaction product of an oil and an unsaturated compound

35 The drawback of these resins is the release of acrolein upon oxidative drying, because acrolein is injurious to health.

- 2 -

The water-soluble and air-drying resin according to the present invention is characterized in that the resin comprises substantially units of:

- A. a monoether of a polyethylene glycol having 5-100 ethylene oxide units per molecule, and
- 5 B. the reaction product of
- B1) one or more unsaturated fatty acids or one or more polyalcohol(s) esterified with unsaturated fatty acids with
- 10 B2) an  $\alpha,\beta$ -ethylenically unsaturated carboxyl compound wherein the molar ratio of A:B being from about 0.2:1 to about 4:1.

Given the drawbacks associated with prior water-soluble resins, the present invention provides properly 15 processable, air-drying and water-soluble resins which are suitable as dispersants. These resins result in coatings having desired properties such as for example a good gloss. A further important advantage of the resins according to the 20 present invention is that they do not release acrolein while drying.

The preferred molar ratio of A:B is about 1:1.

The reaction product of one or more unsaturated fatty acids or one or more polyalcohol(s) esterified with unsaturated fatty acids is generally indicated as an oil.

25 The monoether of polyethylene glycol is for example an alkyl ether, an aryl ether or an alkylaryl ether. Preferably the ether is an alkyl ether. Monoethers of polyethylene glycol have at one side a hydroxyl group remaining, which can react with the carbonyl compound.

30 In general, the alkyl group in the alkyl ether has between 1 and 18 carbon atoms, and preferably between 1 and 4 carbon atoms. The alkyl ether of polyethylene glycol can be for example, methoxy, propoxy or butoxy polyethylene glycol. Other suitable alkyl groups include, for example, an octyl-, 35 lauryl- ( $C_{12}$ ) and a cetyl- ( $C_{16}$ ) group.

Preferably, component A is a methoxy polyethylene glycol having 8 to 20 ethylene oxide units per molecule.

- 3 -

The polyethylene glycol (PEG) can be used in a form in which one or more fragments of polypropylene glycol (PPG) are linked to the PEG. Such a molecule is called a block polymer. The PPG/PEG ratio can be set as desired, taking into account the water solubility of the resin. Generally, 70-95% of the block copolymer will be PEG, and preferably 80-90%. If the alkyl group is a methyl group, this results in a methoxy polypropylene glycol/polyethylene glycol block polymer a methoxy polyethylene glycol/polypropylene glycol block copolymer. Preferably the polyethylene glycol has 8-20 alkoxide units per molecule. More preferably, the polyethylene glycol has 10-16 alkoxide units per molecule. The number of alkoxide units per molecule is chosen so that the resin is water soluble.

Suitable unsaturated fatty acids esterified with polyalcohols include, for example, linseed oil, soybean oil, safflower oil, oiticica oil, caraway oil, rapeseed oil, wood oil and fish oil. It is also possible to use diesters and triesters of polyalcohols, such as glycerol, triméthylol propane or pentaerythritol. And as unsaturated fatty acids, tall oil fatty acid and the fatty acids of the above-mentioned unsaturated oils can be used.

Preferably, the  $\alpha,\beta$ -ethylenically unsaturated carboxyl compound is a carboxyl compound, such as, for example, (meth)acrylic acid or cinnamonic acid. More preferably, the compound is a dicarboxylic compound such as for example maleic acid, fumaric acid, itaconic acid, citraconic acid and mesaconic acid. Most preferably, the  $\alpha,\beta$ -ethylenically unsaturated carboxyl compound is an anhydride, such as for example maleic anhydride, itaconic acid anhydride or citraconic anhydride.

Preferably the  $\alpha,\beta$ -ethylenically unsaturated carboxyl compound is a maleic anhydride.

According to a preferred embodiment of the present invention, component B is the reaction product of linseed oil and/or safflower oil with maleic anhydride.

Thus, a low-viscosity, easily processable, air-

- 4 -

drying and water-soluble resin is obtained. If used as a paint dispersant, this resin results in a paint with desirable properties such as for example a good gloss and a good water resistance. The resin results also in good pigment 5 wetting properties with respect to organic and inorganic pigments.

Moreover, this resin need not be combined with compounds such as for example amines or organic solvents. In other words, a solvent-free system is obtained.

10 Another advantage of the use of the resin as dispersant is the minimis foaming of the dispersant during the preparation of the paint. Consequently little or no anti-foaming agents are required.

The resin according to the present invention is 15 very suitable for use as a dispersant if it has the following characteristics:

- (1) a number-average molecular weight  $M_n$  of between 1000 and 4000;
- (2) a weight-average molecular weight  $M_w$  of between 2000 and 20 8000;
- (3) a polydispersity  $M_w/M_n$  of between 1.5 and 3.5;
- (4) a viscosity higher than 3 dPa.s at 23°C. More preferably, the viscosity is higher than 5 dPa.s. The resin can also be solid or waxy, depending upon the 25 molecular weight. When there are 16 or more ethylene oxide units, the resin will be more or less waxy; and
- (5) a iodine value of between 50 and 150 g iodine/100 g resin.

The molecular weights have been determined by means 30 of GPC (Ultrastyragel, Waters, 100Å, 1000Å, 10,000Å separating capacity  $M_w$  200-300,000).

The viscosity has been determined at 23°C using a rotational viscosimeter (DIN 53019, Bohlin).

35 The iodine value has been determined by means of ASTM D 1959-85.

Since the polydispersity of the resin is between 1.5 and 3.5, hardly any preferential adsorption of high-

- 5 -

molecular weight product takes place.

The present invention also relates to a process for preparing the resins described above as being substantially made up of components A and B.

5 According to a preferred embodiment of the invention, in a first reaction step, component B is prepared by means of an addition reaction of an  $\alpha,\beta$ -ethylenically unsaturated carbonyl compound, preferably maleic anhydride, with an unsaturated vegetable oil (i.e., linseed oil or 10 safflower oil), at a temperature above about 150°C. These two components provide the best results when present in an approximately equimolar quantity. In a second step, compound A is added, and the esterification reaction is carried out. Generally, the molar ratio of A:B is from about 4:1 to about 15 1:4 and is preferably about 1:1.

The resins according to the present invention also include modified resins which are based on the present resin.

20 The acid groups of the resin can, for example, be modified by neutralizing the remaining acid groups with, for instance, hydroxides, oxides, acetates or salts of metals from Groups IA, IIA, IIB of the Periodic Table. Metals from these groups include, among others, Li, Co, V, Zr, Na, K, Ca, Mg and Zn. This process can be performed at room temperature.

25 This modification can also take place by esterifying the acid groups with a compound chosen from the groups consisting of alkoxy polyethylene glycols, monofunctional C<sub>2</sub>-C<sub>16</sub> epoxy compounds, glycidyl (meth)acrylate, hydroxyalkyl sulphonic acids, aminoalkyl sulphonic acids, hydroxyalkyl phosphonic acids or aminoalkyl phosphonic acids at a suitable temperature, for instance 150-180°C.

30 Glycidyl (meth)acrylate should preferably be used at a temperature lower than 150°C so as to prevent the acrylate group from reacting. A catalyst can optionally be used with the glycidyl (meth)acrylate. Suitable catalysts include, for example, triethylamine and N,N-dimethylaniline. Suitable examples of hydroxyalkyl sulphonic acids include for

- 6 -

example 2-hydroxyethyl sulphonic acid, p-hydroxybenzene sulphonic acid or aminoalkyl sulphonic acids, such as 1-aminobutane sulphonic acid-4 and p-aminobenzene sulphonic acid.

5       Also, propylene oxide or butylene oxide can be used as modifying agent.

It is also possible to neutralize the acid group with NH<sub>4</sub>OH or an amine. Although such neutralization is within the scope of the present invention, it can have the  
10     disadvantage of creating undesirable environmental effects.

The molar ratio of the reactants in the modification reaction is substantially 1:1.

The resin according to the present invention can be used, for example, as a dispersant, a grinding agent and a  
15     wetting agent for pigments in combination with alkyd resins, epoxy ester resins and polymer emulsions.

A suitable pigment pasta contains, for instance, 50-70% wt.% pigment, 3-7% wt.% resin according to the present invention and 20-45% wt.% water.

20       The use of the resin according to the present invention as an air-drying, water-soluble dispersant results in a substantially improved solubility and compatibility with, for instance, alkyd emulsions. In this way, systems with a good gloss are obtained.

25       The resin according to the present invention can also be used as a water-soluble and air-drying binder.

Another possibility of the resin is the use in a water-soluble wood preservative as a vehicle. When used in a wood preservative, it is used instead of so-called Wolman  
30     salts against rotting. A side effect is that the resin according to the invention has a water repellent effect. This will enhance the dimensional stability of wood (as measured by its water uptake).

35       The resin according to the present invention can also be used as an air-drying plasticizer in, for instance, acrylate dispersions. Traditional coalescing agents for acrylate dispersions include, for instance, (others of)

- 7 -

ethylene and propylene glycols. These compounds, however, evaporate during the drying of a film, which is undesirable for the environment. The resin according to the present invention does not possess this disadvantage.

5 Another use of the resin according to the present invention is as a drying emulsifier for the preparation of alkyd emulsions and in acrylate dispersions.

10 The resin according to the present invention can be mixed with the customary additives for obtaining paint compositions. Suitable additives include, for example, pigments, colorants, fillers, thickeners, flow-promoting agents, thixotropic agents, flattening agents, stabilizers and siccatives.

15 The present invention is elucidated by means of the following non-restrictive examples.

#### Example I

##### Preparation of a resin

20 In a four-necked flask provided with a nitrogen feed system, mechanical stirrer, thermocouple and dropping funnel, 98 parts by weight maleic anhydride was added at 215°C to 878 parts by weight linseed oil and stirred at 215°C until no reflux of maleic anhydride was visible any more. The resulting product (component B) was an oil-like, low-viscosity liquid with a total acid number of 115 mg KOH/g sample.

25 Subsequently, 750 parts by weight methoxy polyethylene glycol having 16 ethylene oxide units per molecule (component A) was added to this product. Next, the mixture was kept at the same temperature for several hours.

After cooling, a water-soluble waxy product having the following properties was obtained:

* solids content:	100%
* iodine value:	110 g I <sub>2</sub> /100 g product
35 * acid number:	35 mg KOH/g product
* viscosity (23°C):	waxy

- 8 -

Example II and Comparative Experiment APreparation of a Paint

In a Cowless dissolver, a pigment paste based on a dispersant, titanium dioxide, thickener and demineralized water was prepared in 30 minutes at 3000 rpm, according to Table I below.

TABLE I

		A	II
10	Resin according to Example I	--	0.60
	Orotan 731 <sup>R</sup> , 25% <sup>1)</sup>	0.65	0.65
	Demineralized water	9.30	14.80
15	Borchigen DFN <sup>R</sup> /demineralized water 1:2 <sup>2)</sup>	5.00	--
	Kronos 2190 <sup>R</sup> <sup>3)</sup>	30.02	30.20
	Agitan 295 <sup>R</sup> <sup>4)</sup>	0.10	0.10
	<b>Dispersion in pearl mill</b>		
20	Premix:		
	Uradil XP 516 AZ <sup>R</sup> <sup>5)</sup>	49.40	49.40
	Acrysol RM 8 <sup>R</sup> <sup>6)</sup>	0.75	0.50
	Siccatol 938 <sup>R</sup> <sup>7)</sup>	1.50	1.50
	Urad DD 81 <sup>R</sup> <sup>8)</sup>	0.25	0.25
25	<b>Adding pigment paste to premix</b>		
	Addition of:		
	Acrysol RM 8 <sup>R</sup>	1.20	0.35
	Acrysol RM 1020 <sup>R</sup> <sup>9)</sup>	0.60	0.60
30	Fluorad FC 129 <sup>R</sup> /Water (10%) <sup>10)</sup>	1.05	1.05
	Pigment-volume concentration, %	20	19.6
	Solids content, %	60.7	61.3
	Viscosity 23°C (DIN 53019), dPa.s	30	20
	pH	7.00	7.30

- 9 -

		A	II
BK drying time, stage 1, min	<sup>11)</sup>	20	40
BK drying time, stage 2, min	<sup>11)</sup>	150	100
BK drying time, stage 3, min	<sup>11)</sup>	650	220
BK drying time, stage 4, min	<sup>11)</sup>	1100	950
5	Gloss 20°	83	95
	Gloss 60°	95	90
	Hardness(s), 1 day	27	28
	Hardness(s), 1 week	38	40
	Adhesion to wood <sup>12)</sup>	3	3
10	Adhesion to alkyd <sup>12)</sup>	5	5
	Water resistance, after 1 week <sup>12)</sup>	4	4
	Adhesion wood, after 1 week <sup>12)</sup>	5	5
	Adhesion alkyd, after 1 week <sup>12)</sup>	5	5

15

1) Orotan 73<sup>R</sup>: dispersant, isobutylene maleic acid copolymer, Na salt  
2) Borchigen DFN<sup>R</sup>: pigment wetting agent  
3) Kronos 2190<sup>R</sup>: titanium dioxide  
20 4) Agitan 295<sup>R</sup>: anti-foaming agent  
5) Uradil XP516A2<sup>R</sup>: alkyd emulsion of DSM Resins  
6) Acrysol RM8<sup>R</sup>: polyurethane thickener  
7) Siccatal 938<sup>R</sup>: siccative mixture  
8) Urad DD81<sup>R</sup>: anti-skinning agent  
25 9) Acrysol RM1020<sup>R</sup>: polyurethane thickener  
10) Fluofad FC129<sup>R</sup>: flow-promoting agent  
11) The drying time was determined by means of a BK drying recorder (BYK-Chemie no. 270, Mickle Laboratory Engineering Co., Gomshall, Surrey, England)  
30 6) Visual assessment with the following rating:  
1 = unacceptable  
2 = insufficient  
3 = sufficient  
4 = good  
35 5 = excellent

Table I demonstrates that the gloss is improved considerably if instead of Borchigen DFN®, the resin according to the present invention is used. Moreover, the other desired properties are preserved when the resin according to the present invention is employed.

- 10 -

WHAT IS CLAIMED IS:

1. A water-soluble and air drying resin, comprising substantially units of
  - A. a monoether of a polyethylene glycol having 5-100 ethylene oxide units per molecule, and
  - B. the reaction product of:
    - B1) one or more unsaturated fatty acids or one or more polyalcohol(s) esterified with unsaturated fatty acids with
    - B2) an  $\alpha,\beta$ -ethylenically unsaturated carboxyl compound wherein the molar ratio of A:B is from about 0.2:1 to about 4:1.
- 15 2. A resin according to claim 1, wherein said monoether is an alkyl-, aryl- or alkylaryl ether.
3. A resin according to any one of claims 1-2, wherein the monoether contains 8-20 ethylene oxide units per molecule.
- 20 4. A resin according to any one of claims 1-3, wherein B is the reaction product of linseed oil and/or safflower oil with maleic anhydride.
5. A process for preparing a water-soluble and air-drying resin according to any one of claims 1-4, comprising the steps of:
  - (1) preparing component B by means of an addition reaction of an  $\alpha,\beta$ -ethylenically unsaturated carboxyl compound with an unsaturated vegetable oil at a temperature above 150°C, and
  - 30 (2) reacting component B with a component A comprising a monoether of a polyethylene glycol having 5-100 ethylene oxide units per molecule, such that the molar ratio of A:B is from about 4:1 to about 1:4.

- 11 -

6. A process according to claim 5 where in in the first step the  $\alpha,\beta$ -ethylenically unsaturated carboxyl compound and the unsaturated vegetable oil are present in an approximately equimolar quantity.
- 5 7. Use of a resin according to any one of claims 1-4 or use of a resin obtained according to any one of claims 5-6.
8. Use of a resin according to any one of claims 1-4 or use of a resin obtained according to any one of claims 5-6 as dispersing agent.
- 10 9. Use of a resin according to any one of claims 1-4 or use of a resin obtained according to any one of claims 5-6 as a vehicle in a wood preservative.
10. Pigment paste comprising a resin according to any one of claims 1-4 or comprising a resin obtained according to any one of claims 5-6.
- 15

## INTERNATIONAL SEARCH REPORT

Int'l. Application No  
PCT/NL 94/00019

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C08G65/32 C08L71/02 C09D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 C08G C08L C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 715 866 (STAKER D.D.) 29 December 1987 see claim 1 see column 3, line 5 - line 48 see column 4, line 28 - line 36 see example 9 -----	1-5,8
A	US,A,4 071 514 (RIBBECKER L.F.) 31 January 1978 see claim 1 see column 2, line 65 - column 3, line 12 -----	1-10
A	GB,A,2 051 096 (IMPERIAL CHEMICAL INDUSTRIES) 14 January 1981 see claim 1; example 1 -----	1-10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
- 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

- 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- '&' document member of the same patent family

1 Date of the actual completion of the international search

3 May 1994

Date of mailing of the international search report

25.05.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentstaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

O'Sullivan, T

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No  
PCT/NL 94/00019

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4715866	29-12-87	NONE		
US-A-4071514	31-01-78	AU-A-	3372878	06-09-79
		CA-A-	1105191	14-07-81
		DE-A-	2809934	23-11-78
		FR-A-	2391257	15-12-78
		GB-A-	1595738	19-08-81
		JP-A-	54016539	07-02-79
		NL-A-	7805423	22-11-78
GB-A-2051096	14-01-81	EP-A,B	0012524	25-06-80
		US-A-	4273888	16-06-81

